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(54) Title: PHOTOSENSITIVE FLUORINATED POLY(AMIC ACID) AMINOACRYLATE SALT			
(57) Abstract			
<p>A photosensitive composition of a fluorinated poly(amic acid) neutralized with a tertiary amine di(meth) acrylate useful for forming relief structures on electrical devices such as capacitors, integrated circuits, printed circuits and semiconductors. A solution of the composition is applied to a substrate such as a coated silicon wafer, which is the base for an electric device; dried to form a film; the film is exposed to radiation through a pattern and photopolymerized; the unexposed and unpolymerized part of the film is dissolved off; and the resulting relief structure is converted to a polyimide structure having sharp image definition, transparency and low moisture absorption and dielectric constant.</p>			

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TITLEPHOTOSENSITIVE FLUORINATED POLY(AMIC ACID)  
5 AMINOACRYLATE SALTBACKGROUND OF THE INVENTION

- This invention relates to a photosensitive composition derived from a fluorinated poly(amic acid) which has been partially neutralized with a tertiary amine di(meth)acrylate, especially N-methyldiethanolamine dimethacrylate, for use in forming relief structures on electrical or electronic devices such as semiconductors, capacitors and printed circuits.
- 15 Photopolymerizable polymeric compositions used to form relief structures on electrical devices are well known. Also, photosensitive poly(amic acid) derivatives, which produce thermally stable polyimide films upon curing, have been widely employed for this purpose. Directly 20 patternable photosensitive polyimides simplify relief structure construction in semiconductor manufacture by eliminating conventional photoresists and their attendant processing steps. Negative working photoactive functional groups can be incorporated into polyimide precursors as 25 poly(amic acid) esters. These photoactive functional groups include acrylate, methacrylate, allyl, vinyl, and related double bond containing structures which can be photopolymerized.
- Application of the described photosensitive polyimide 30 precursors or photoresists involves coating a solution of these materials onto a substrate, such as a silicon wafer, and drying to form a film. The film is then exposed to radiation through a masking template and photopolymerized. Unexposed regions, which remain soluble, are removed with a 35 developer solution, leaving behind a relief structure. Thermal curing of the relief structure converts the

photopolymerized material into a polyimide coating with pattern definition.

Whereas most photosensitive poly(amic acid) ester resins are developable after exposure by a range of techniques, including spray, puddle and immersion development, the photosensitive poly(amic acid) salts most widely employed, process best with poly(amic acid)s which are readily soluble in the common process solvents, such as, for example, N-methyl-2-pyrrolidone, dimethyl acetamide, dimethyl formamide, and dimethyl sulfoxide, and frequently require prolonged immersion or puddle development methods with the commonly employed developers, which usually are composed of various N-methyl-2-pyrrolidone, alcohol, water mixtures. Poly(amic acid) dialkylamine acrylate and methacrylate salts, in particular, generally require slow immersion or batch type development for optimum pattern resolution, and therefore are mainly limited to readily soluble poly(amic acid) systems, in order to be commercially processable.

Moreover, slow development rates make continuous spray equipment impractical for many poly(amic acid) salt formulations. Slow development also hinders the use of less soluble, rigid poly(amic acid)s as their photosensitive dialkylamine acrylate or methacrylate salts.

Thus, the desirable features of rigid polyimide structures, such as low thermal expansion, low stress, and excellent mechanical properties, are not readily attainable as a processable photosensitive amine salt precursor. Therefore, a need persists for photosensitive salts of rigid, less soluble polyamic acids which can be conveniently processed to well-resolved, patterned polyimide coatings on different substrates, and especially electronic devices.

Japanese Patent Application 3-91752, published on April 17, 1991, discloses a photosensitive composition comprising a poly(amic acid), a polyfunctional

aminoacrylate containing two or three acrylate or methacrylate groups and a sensitizing agent.

Japanese Patent Application 3-206454, published on September 9, 1991, discloses a photosensitive composition comprising a poly(amic acid) containing up to 50 weight % of a copolymerized silicone diamine monomer, a polyfunctional aminoacrylate containing two or three acrylate or methacrylate groups, a biscoumarin sensitizer and a glycine photoinitiator.

Japanese Patent Application 3-206455, published on September 9, 1991, discloses a photosensitive composition comprising a poly(amic acid) containing up to 50 weight % of a copolymerized silicone diamine monomer, a polyfunctional aminoacrylate containing two or three acrylate or methacrylate groups, a biscoumarin sensitizer and an oxazolone initiator.

The photosensitive composition of the invention, derived from a fluorinated poly(amic acid) and a tertiary amine di(meth)acrylate, is highly sensitive to actinic radiation and is directly patternable by exposure. The resulting films are more transparent, have better adhesion, are more rapidly developable, and have lower dielectric constant and water absorption than the prior art photosensitive compositions derived from unfluorinated poly(amic acid)s.

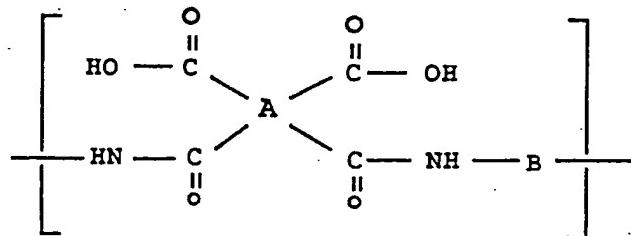
#### SUMMARY OF THE INVENTION

The present invention relates to a photosensitive composition used for forming relief polyimide structures on electrical devices such as, for example, semiconductors, capacitors or printed circuits. The compositions of the present invention can be used to prepare coatings which are readily patterned by photopolymerization using actinic radiation. Formulations containing fluorinated poly(amic acid)s and the tertiary amine di(meth)acrylate monomers of this invention provide well-resolved negative images which

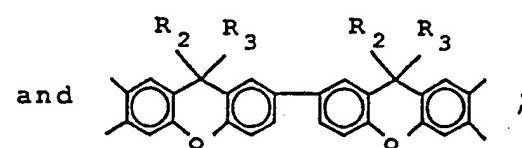
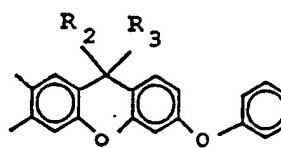
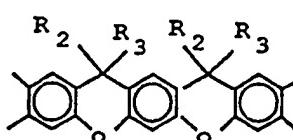
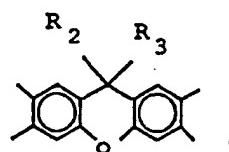
can be smoothly developed. Thermal curing provides a durable polyimide patterned coating with mechanical, electrical and chemical properties useful in electrical device manufacture.

5 More particularly, this invention relates to a photosensitive composition and an electronic device derived therefrom comprising:

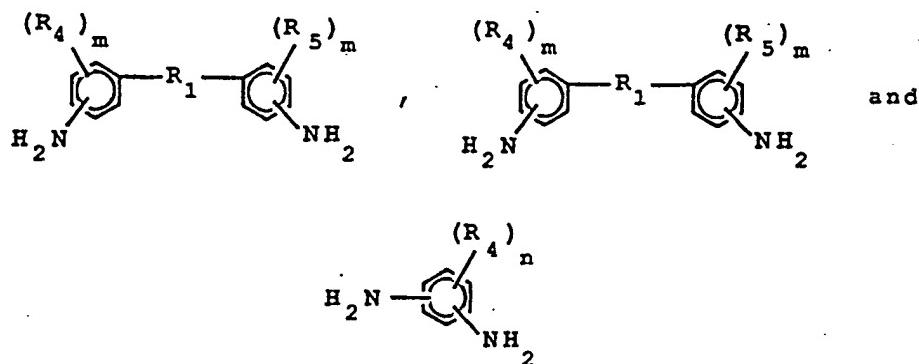
- 10 (a) an aprotic solvent;  
(b) a photosensitizing component;  
(c) a fluorinated poly(amic acid) polymer containing  
a repeating unit of the formula



15 wherein A is a tetravalent organic radical selected from the group consisting of



and B is a divalent radical of an aromatic diamine selected from the group consisting of



wherein R<sub>1</sub> is -CH<sub>2</sub>-, -C<sub>2</sub>H<sub>4</sub>, -C(CF<sub>3</sub>)<sub>2</sub>-,  
 5 -C<sub>4</sub>-7F<sub>8</sub>-14-, -S-, -SO<sub>2</sub>-, -O-, -CO-,  
 R<sub>6</sub>, -O-R<sub>6</sub>-O-, -O-R<sub>6</sub>-C(CF<sub>3</sub>)<sub>2</sub>-R<sub>6</sub>-O-,  
 -O-R<sub>6</sub>-C(CH<sub>3</sub>)<sub>2</sub>-R<sub>6</sub>-O-, -O-R<sub>6</sub>-SO<sub>2</sub>-R<sub>6</sub>-O-,  
 -O-R<sub>6</sub>-O-R<sub>6</sub>-O-, -O-R<sub>6</sub>-CO-R<sub>6</sub>-O-,  
 -O-R<sub>6</sub>-CO-R<sub>6</sub>-CO-R<sub>6</sub>-O-, -O-R<sub>6</sub>-R<sub>6</sub>-O-, -CO-R<sub>6</sub>-CO-,  
 10 -CO-R<sub>6</sub>-O-R<sub>6</sub>-CO- or -O-R<sub>6</sub>-SO<sub>2</sub>-R<sub>6</sub>-O-;

R<sub>2</sub> and R<sub>3</sub> are phenyl, C<sub>1</sub>-4 alkyl,  
 C<sub>1</sub>-4 perfluoralkyl, C<sub>1</sub>-4 perfluoroalkoxy,  
 C<sub>1</sub>-4 perfluoroalkylphenyl or -OC<sub>1</sub>-6 alkylene-  
 15 OC<sub>1</sub>-6 perfluoroalkyl;

R<sub>4</sub> and R<sub>5</sub> are H, Cl, F, C<sub>1</sub>-4 alkyl, OH;  
 C<sub>1</sub>-8 perfluoroalkyl or C<sub>1</sub>-8 perfluoroalkoxy;

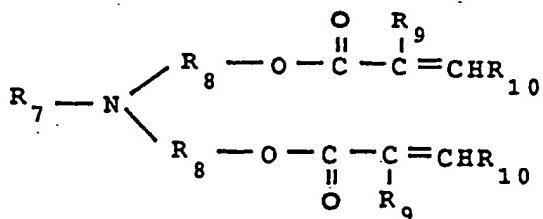
20 R<sub>6</sub> is



m is 0 to 4; and

25 n is 0 to 3; and

(d) a tertiary amine di(meth)acrylate having the formula



wherein R<sub>7</sub> is C<sub>1-6</sub> alkyl or C<sub>1-3</sub> cycloalkyl;  
5 R<sub>8</sub> is C<sub>2-12</sub> alkylene or C<sub>3-6</sub> cycloalkylene;  
R<sub>9</sub> is H or C<sub>1-2</sub> alkyl; and R<sub>10</sub> is H or aryl,

wherein said tertiary amine di(meth)acrylate is present in an amount sufficient to neutralize from 10 to 100 mole % of said poly(amic acid) polymer.

Most preferably, the photosensitive composition of the invention comprises a fluorinated poly(amic acid) neutralized with methyl diethanolamine dimethacrylate.

## DETAILED DESCRIPTION OF THE INVENTION

The photosensitive composition of the present invention comprises (a) an aprotic solvent, (b) a photosensitizing component, (c) a fluorinated poly(amic acid) polymer and (d) a tertiary amine di(meth)acrylate and is used to form relief structures on electrical or electronic devices such as capacitors and semiconductors. The composition is applied to a substrate such as a silicon wafer and dried to form a film on the substrate. The film is then exposed to actinic radiation through a masking template (pattern) and photopolymerized. The unexposed and unpolymerized part of the film is dissolved off with a developer solution to form a relief structure. The resulting relief structure is baked to remove the material not stable to heat and to form a polyimide structure with a sharp definition and with good mechanical, chemical and electrical properties.

Poly(amic acid) Preparation

Poly(amic acid) preparation and conversion to polyimides is performed by general procedures well known in the art and described in references such as *Polyimides*, D. Wilson, H. D. Stenzenberger and P. M. Hergenrother ed., Blackie & Sons, London, 1990, pp. 1-35; *Polyimides: Thermally Stable Polymers*, M. I. Bessanov, et al., 2nd edn., Plenum, New York (1987), pp. 1-95.

Solutions of aromatic diamines such as 4,4'-diaminodiphenyl ether in N-methylpyrrolidone, or other aprotic solvents listed below, are reacted with tetracarboxylic dianhydrides, such as 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride, at 1.0-0.50 stoichiometric ratios, affording 10-30 weight % poly(amic acid) solutions after suitable reaction. The poly(amic acid)s produced range in weight average molecular weight from 10,000-350,000, as determined by gel permeation chromatography versus a polystyrene reference. The reaction masses are pressure filtered through 0.1-10 micron filters before isolation.

Either the tetracarboxylic dianhydride and/or the aromatic diamine component can be fluorinated. At least 5 mole % of the fluorinated tetracarboxylic dianhydride and/or the fluorinated aromatic diamine, based on the total molar amount of dianhydride and diamine components present in the polymer, is required to obtain the requisite transparency, adhesion, rapid development, low dielectric strength and water absorption characteristic of the polyimide. Accordingly, other additional unfluorinated aromatic tetracarboxylic dianhydrides and/or aromatic diamines may be included in amounts which will not appreciably degrade the desirable properties of the polyimide.

Fluorinated aromatic diamines which are suitable for use in the present invention include, but are not limited to:

- 5        2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane,  
          2,2-bis(4-aminophenyl)hexafluoropropane,  
          2,2-bis(4-amino-3-hydroxyphenyl)hexafluoropropane,  
          1,3-bis(4-aminophenyl)hexafluoropropane,  
          1,4-bis(4-aminophenyl)octafluorobutane,  
          1,5-bis(4-aminophenyl)decafluoropentane,  
10        1,7-bis(4-aminophenyl)tetradecafluoroheptane,  
          2,2-bis[4-(3-aminophenoxy)phenyl]hexafluoropropane,  
          2,2-bis[4-(2-aminophenoxy)phenyl]hexafluoropropane,  
          2,2-bis[4-(4-aminophenoxy)-3,5-dimethylphenyl]-  
          hexafluoropropane,  
15        2,2-bis[4-(4-aminophenoxy)-3,5-bis(trifluoromethyl)-  
          phenyl]hexafluoropropane,  
          1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene,  
          4,4'-bis(4-amino-2-trifluoromethylphenoxy)biphenyl,  
          4,4'-bis(4-amino-3-trifluoromethylphenoxy)biphenyl,  
20        4,4'-bis(4-amino-2-trifluoromethylphenoxy)diphenyl  
          sulfone,  
          4,4'-bis(3-amino-3-trifluoromethylphenoxy)diphenyl  
          sulfone,  
          2,2-bis[4-(4-amino-3-trifluoromethylphenoxy)phenyl-  
25        hexafluoropropane,  
          5,5'-oxy-bis[3-(trifluoromethyl)benzenamine],  
          4,4'-oxy-bis[3-(trifluoromethyl)benzenamine],  
          4,5'-oxy-bis[3-(trifluoromethyl)benzenamine],  
          2,2-bis(3-aminophenyl)hexafluoropropane,  
30        4,4'-diaminoctafluorobiphenyl,  
          4,4'-diamino-2,2'-bis(trifluoromethyl)biphenyl,  
          4,4'-diamino-3,3'-dimethylhexafluorobiphenyl,  
          4,4'-diamino-2,2'-bis(trifluoromethoxy)biphenyl,  
          4,4'-diamino-2,2'-bis(perfluoro-2-hydro-3-  
35        oxahexyloxy)-biphenyl,

- 4,4'-diamino-2,2'-bis(1,1,2,2-tetrafluoroethoxy)biphenyl,  
5,5'-diamino-2,2'-bis(trifluoromethyl)biphenyl,  
5,5'-diamino-3,3'-bis(trifluoromethyl)biphenyl,  
5 5,5'-diamino-2,2'-bis(trifluoromethoxy)biphenyl,  
3,5-diaminobenzotrifluoride,  
2,5-diaminobenzotrifluoride,  
2,4,6-trimethyl-3,5-diaminoheptadecylfluoroctyl  
benzene, and  
10 3,5-diaminoheptadecylfluoroctyl benzene.

Fluorinated aromatic tetracarboxylic dianhydrides which are suitable for use in the present invention include, but are not limited to,

- 15 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride,  
9,9-bis(trifluoromethyl)xanthene 2,3,6,7-tetracarboxylic dianhydride,  
9-trifluoromethyl-9-phenylxanthene 2,3,6,7-tetracarboxylic dianhydride,  
20 9-pentafluoroethyl-9-phenylxanthene 2,3,6,7-tetracarboxylic dianhydride,  
9-heptafluoropropyl-9-phenylxanthene 2,3,6,7-tetracarboxylic dianhydride,  
25 9-trifluoromethyl-9-(trifluoromethylphenyl)xanthene 2,3,6,7-tetracarboxylic dianhydride,  
9-trifluoromethyl-9-methyl xanthene 2,3,6,7-tetracarboxylic dianhydride,  
9-phenyl-9-trifluoromethyl-3-(3,4-dicarboxy anhydridophenoxy)-xanthene-6,7-dicarboxylic anhydride,  
30 12,14-diphenyl-12,14-bis(trifluoromethyl)-12H,14H-5,7-dioxapentacene-2,3,9,10-tetracarboxylic dianhydride,  
12,14-diphenyl-12,14-bis(pentafluoroethyl)-12H,14H-5,7-dioxapentacene-2,3,9,10-tetracarboxylic  
35 dianhydride,

12,14-diphenyl-12,14-bis(heptafluoropropyl)-12H,14H-  
5,7-dioxapentacene-2,3,9,10-tetracarboxylic  
dianhydride,

5       5,12-diphenyl-5,12-bis(trifluoromethyl)-5H,12H-7,14-  
dioxapentacene-2,3,9,10-tetracarboxylic dianhydride,  
and (9-phenyl-9-trifluoromethyl-6-7-dicarboxy-  
anhydrido)-2,2'-bixanthyl.

Fluorinated aromatic diamines and fluorinated aromatic  
10 tetracarboxylic dianhydrides that are suitable for use in  
the invention are more fully described in U.S. 3,310,573,  
U.S. 5,097,000, U.S. 5,153,336, U.S. 5,189,138, U.S.  
5,145,999, U.S. 5,177,179 and U.S. 5,175,367, the  
disclosures of which are hereby incorporated by reference.

15       Additional unfluorinated aromatic diamines and  
aromatic tetracarboxylic dianhydrides that can be used in  
the invention include, but are not limited to:

4,4'-diaminodiphenylether,

3,3'-diaminodiphenylether,

20       3,4'-diaminodiphenylether,

4,4'-diamino-3,3'-dimethylbiphenyl,

4,4'-diamino-3,3'-dimethoxybiphenyl,

4,4'-bis(4-aminophenoxy)biphenyl,

4,4'-diaminodiphenylsulfone,

25       3,3'-diaminodiphenylsulfone,

bis[4-(4-aminophenoxy)phenyl]sulfone,

bis[4-(3-aminophenoxy)phenyl]sulfone,

bis[4-(2-aminophenoxy)phenyl]sulfone,

1,4-bis(4-aminophenoxy)benzene,

30       4,4'-diamino-2,2'-dichloro-5,5'-dimethoxybiphenyl,

4,4'-diamino-2,2',5,5'-tetrachlorobiphenyl,

o-tolidine sulfone,

1,3-bis(4-aminophenoxy)benzene,

1,3-bis(3-aminophenoxy)benzene,

35       1,4-bis(4-aminophenyl)benzene,

[4-(4-aminophenoxy)phenyl]ether,

bis(4-aminophenyl)methane,  
bis(4-amino-3-ethylphenyl)methane,  
bis(4-amino-3-methylphenyl)methane,  
bis(4-amino-3-chlorophenyl)methane,  
5 bis(4-aminophenyl)sulfide,  
1,3-diaminobenzene  
2,2-bis[4-(4-aminophenoxy)phenyl]propane,  
2,2-bis(4-aminophenyl)propane,  
2,2-bis(4-amino-3-hydroxyphenyl)propane,  
10 4,4'-diamino-3,3'-dichlorobiphenyl,  
4,4'-diamino-3,3'-dihydroxybiphenyl,  
4,4'-diaminobiphenyl,  
bis(3-amino-4-methylphenyl)sulfone,  
2-(4-aminobiphenyl)-2-[3-(4-aminophenoxy)phenyl]-  
15 propane,  
bis(4-amino-2,6-methylphenyl)methane,  
2,4-diamino-1-isopropylbenzene,  
1,4-diamino-2,5-dichlorobenzene,  
1,4-diamino-2,6-dichlorobenzene,  
20 1,4-diamino-2,5-dimethylbenzene,  
1,4-diamino-2-chlorobenzene,  
1,3-diamino-4-chlorobenzene,  
1,4-diamino-5-chloro-2-methylbenzene,  
1,4-diamino-2,3,5,6-tetramethylbenzene,  
25 1,3-diamino-2,4,6-trimethylbenzene,  
1,4-diaminobenzene,  
1,2-bis(4-aminophenyl)ethane,  
2,4-diaminotoluene,  
1,3-diamino-5-trifluoromethylbenzene,  
30 4,4'-diamino-3,3',5,5'-tetramethylbiphenyl,  
4,4'-diamino-2,2'-dimethylbiphenyl,  
1,3-diamino-5-tert-butylbenzene,  
1,4-bis(3-aminophenoxy)benzene,  
bis[4-(3-aminophenyl)phenyl]ether,  
35 4,4'-diamino-2,2'-dichlorobiphenyl,  
3,3'-diamino-4,4'-dihydroxybiphenyl,

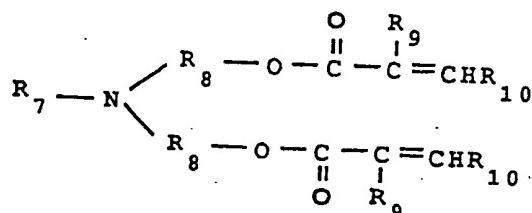
pyromellitic dianhydride,  
3,3',4,4'-biphenyltetracarboxylic dianhydride,  
2,2'3,3'-biphenyltetracarboxylic dianhydride,  
3,3',4,4'-benzophenonetetracarboxylic dianhydride,  
5 2,2-bis(3,4-dicarboxyphenyl)propane dianhydride,  
bis(3,4-dicarboxyphenyl)sulfone dianhydride,  
terphenyltetracarboxylic dianhydride,  
1,1-bis(2,3-dicarboxyphenyl)ethane dianhydride,  
1,1-bis(3,4-dicarboxyphenyl)ethane dianhydride,  
10 bis(2,3-dicarboxyphenyl)methane dianhydride,  
bis(3,4-dicarboxyphenyl)methane dianhydride, and  
oxydiphthalic dianhydride.

Aprotic Solvent

15 Suitable solvents for carrying out the polymerization reaction include, but are not limited to, aprotic or polar organic solvents, such as sulfoxide type solvents including dimethylsulfoxide, diethylsulfoxide, and the like, formamide type solvents, such as N,N-dimethylformamide,  
20 N,N-diethylformamide; acetamide type solvents, including N,N-dimethylacetamide, N,N-diethylacetamide; pyrrolidone type solvents, including N-methyl-2-pyrrolidone, N-cyclohexyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone, N-vinyl-2-pyrrolidone; ether solvents such as ethylene glycol dimethyl ether and diethylene glycol dimethyl ether; phenolic solvents, including phenol, o-, m-, and p-cresol, xlenol, halogenated phenol, catechol;  
25 hexamethylphosphoramide; and a number of lactones including gamma-butyrolactone. These solvents may be used alone or  
30 as a mixture. Partial use of aromatic hydrocarbons such as xylene and toluene is also possible, and sometimes desirable, when, for example, removal of water as an azeotrope is desired.

## Formation of the Photosensitive Poly(amic carboxylate salt)

The tertiary amine di(meth)acrylate is added to the poly(amic acid) solution in order to form a photosensitive poly(amic carboxylate) salt. Poly(amic acid) neutralization by the tertiary amine di(meth)acrylate employed in this invention may represent from 5 to 150 mole % of the theoretically available carboxylic acid groups present. Preferably from 10 to 100 mole %, and more preferably from 25 to 75 mole % neutralization, affords good photospeed and processability using tertiary amine di(meth)acrylates of the formula



15

wherein; R<sub>7</sub> is C<sub>1-6</sub> alkyl or C<sub>1-3</sub> cycloalkyl; R<sub>8</sub> is C<sub>2-12</sub> alkylene or C<sub>3-6</sub> cycloalkylene; R<sub>9</sub> is H or C<sub>1-2</sub> alkyl; and R<sub>10</sub> is H or aryl.

Examples of photosensitive amine di(meth)acrylates which may be used include N-methyldiethanolamine dimethacrylate, N-ethyldiethanolamine dimethacrylate, N-butyldiethanolamine dimethacrylate, N-methyldiethanolamine diacrylate, N-ethyldiethanolamine diacrylate, N-n-propyldiethanolamine dimethacrylate, N-n-propyldiethanolamine diacrylate, N-methyldipropanolamine dimethacrylate and N-ethyldipropanolamine dimethacrylate, but are not limited to these compounds. Particularly preferred herein is N-methyldiethanolamine dimethacrylate, which doubles the number of photoactive groups for each pendant carboxylate group, thereby improving photospeed; and decreases the amount of acrylate added to the

photosensitive formulation, thereby improving cured film properties.

Photosensitive Component Formulation

5       Formulation of the photosensitive poly(amic carboxylate salt) with suitable photopolymerization initiators, photosensitizers, hydrogen donors, oxygen scavengers and stabilizers, provides a photosensitive formulation for coating as a photoresist, which may remain  
10      on the device or be removed if so desired.

Typical photopolymerization initiators effective with the formulations described herein include those disclosed by Goff in U.S. Patent No. 4,414,312, and references cited therein, which are hereby incorporated by reference. These  
15      include 2,4,5-triphenyl imidazolyl dimers having an ortho substituent on the 2 phenyl ring, such as 2-(o-chlorophenyl)-4,5-diphenylimidazolyl dimer, 2-(o-fluorophenyl)-4,5-diphenylimidazolyl dimer, 2-(o-methoxyphenyl)-4,5-diphenylimidazolyl dimer, 2-(o-ethoxyphenyl)-4,5-diphenylimidazolyl dimer, and mixtures thereof.  
20      Particularly preferred are bis(2-(o-chlorophenyl)-4,5-diphenylimidazolyl) and bis[2-(o-chlorophenyl)-4,5-di-(m-methoxyphenyl) imidazolyl] since these compounds are stable and are effective polymerization initiators. The initiator  
25      may constitute from 0.01 to 0.25 weight %, preferably 0.07 weight %, of the total formulation.

Photosensitizers employed to increase formulation sensitivity include aromatic ketones also described in U.S. Patent No. 4,414,312 and references cited therein, which  
30      are hereby incorporated by reference, such as benzophenone, 4,4'-bis(dimethylamino)benzophenone, 4,4'-bis(diethylamino)benzophenone, 4-acyloxy-4'-diethylaminobenzophenone. Derivatives of aryl ketones and p-dialkylaminoarylaldehydes as disclosed by Dueber U.S.  
35      Patent No. 4,162,162 which is incorporated by reference. Particularly 2-[9'-(2',3',7'-tetrahydro-1H,5H-benzo[ij]-

quinolylidene)]-5,6-dimethoxy-1-indanone claimed in U.S. Patent No. 4,162,162 is effective in this regard. N-alkylindolylidenes or N-alkylbenzothiazolylidene alkanones disclosed in U.S. Patent No. 4,454,218 which is

- 5 incorporated by reference, and constrained N-alkyl aryl ketones as disclosed by Anderson et al. in U.S. Patent No. 4,535,052, which is herein incorporated by reference. Also 2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-11-oxo-1H,5H,11H-(1)benzopyrano[5,7,8-ij]quinolizine-10-carboxylic acid  
10 ethyl ester is an effective sensitizer in the formulations employed herein. Photosensitive compositions employed contain approximately 0.001 to 0.05 weight %, preferably 0.005 weight %, photosensitizer.

Hydrogen donors/oxygen scavengers critical to  
15 efficient photopolymerization and comprising formulations of this invention include those disclosed in the aforementioned U.S. Patent No. 4,414,312 and references cited therein, which disclosure is hereby incorporated by reference. In particular 2-mercaptopbenzthiazole, 2-  
20 mercaptobenzoxazole and 2-mercaptobenzimidazole are useful. Hydrogen donors/oxygen scavenger compounds comprise 0.01 to 0.25 weight %, preferably 0.06 weight %, of the total photosensitive composition.

- Polymerization inhibitors may be added to improve the  
25 storage stability of the formulation. Examples of such inhibitors include hydroquinone, N-nitrosodiphenyleneamine, and 1,4,4-trimethyl-2,3-diazabicyclo(3.2.2)non-2-ene, 2,3-dioxide as disclosed in U.S. Patent No. 4,168,982. Phenyl pyrazolidinones, and tetramethyldiphenyl quinone as  
30 disclosed in U.S. Patent No. 4,168,982, and mixtures thereof. The quantity of polymerization inhibitors, if added, is usually about 0.001 to 0.01 weight %, preferably 0.002 weight %, of the total photosensitive composition.

- An adhesion promoter may be added to the  
35 photosensitive composition of the invention to improve adhesion between the photopolymerizable resin and the

substrate to which it is applied. Suitable adhesion promoters are the polyfunctional alkoxy silane compounds disclosed by Merriman and Goff in U.S. Patent No.

5,063,115. Adhesion promoter, when added, usually

5 constitutes from 0.01 to 0.20 weight %, preferably 0.02 weight %, of the total photosensitive composition.

Blending of selected components of each type described hereinabove is generally completed by stirring or rolling the mixtures to assure complete dissolution, and then

10 pressure filtering through a 0.1 to 10 micron filter to provide the final photosensitive solution or photoresist, which may be used for substrate coating and further processing.

15                   Application and Processing of the  
                      Photosensitive Composition

The photosensitive composition, or photoresist, is generally coated on silicon, ceramic or similar substrates.

Adhesion promoters may be applied directly to the substrate

20 surface before coating, or introduced as part of the coating formulation as previously described. An aminosilane compound, such as triethoxy silylpropyl urea, is commonly used for this purpose. The photoresist is usually applied by spinning the wafer at 1000-6000 rpm for

25 30 seconds, then prebaking on a hot plate or in a convection oven to partially remove the solvent and produce an approximately 2-50 microns thick film coating. The coated substrate is then exposed to an ultraviolet light source, which is passed through a mask template, using a

30 contact or projection printer. Exposed wafers are subsequently developed by immersion or spraying with a solvent, then rinsed, which removes the unexposed regions of the coating, leaving behind an insoluble polymer relief structure which reproduces the original template. The

35 developer solution can be a mixture of solvents including, but not limited to, N-methyl-2-pyrrolidone,

dimethylsulfoxide, N,N-dimethylformamide, N,N-diethylacetamide, gamma-butyrolactone, ethylene glycol dimethyl ether, methanol, n-butanol, isopropanol and water.

A mixture of N-methylpyrrolidone, methanol and water

5 (62/33/5 weight ratio) was employed for spray development testing of the photoresists of this invention. A final water or isopropanol rinse was used before drying the wafer.

Film retention can be measured by thickness and/or  
10 weight loss. The coating development rate (micrometers per second) of the photoresist can be obtained from this data. Image resolution may be established by optical and scanning electron microscopy of the pattern features.

It is important that each essential property of the  
15 photoresist remains within certain practical limits. The development rate should not be lower than 0.05 micrometer per second, and preferably not be lower than 0.15 micrometer per second. The % film thickness retention at 500 mJ/cm<sup>2</sup> exposure should not be lower than 60%,  
20 preferably not be lower than 80%. The minimum feature size in a 20 micrometers thick soft baked photoresist film should not be greater than 35, and preferably not be greater than 20 micrometers.

The patterned wafer is finally cured at 350°C for 60  
25 minutes in a nitrogen purged convection oven. The curing procedure decomposes the acrylate crosslinkages, expels residual photosensitive components and yields a polyimide film with the relief image permanently fixed on the substrate. The cured film exhibits good pattern  
30 resolution, and good chemical, thermal and mechanical properties.

The photosensitive composition of the invention is derived from a poly(amic acid) containing fluorine partially neutralized with a tertiary amine  
35 di(meth)acrylate, such as methylmethacrylate, diethanolamine dimethacrylate. The incorporation of fluorine into the

polymer increases the transparency of the polyimide and improves its photolithographic performance. In addition, the incorporation of fluorine decreases the moisture absorption and the dielectric constant of the final cured 5 polyimide film, and increases the adhesion of the polyimide to substrates, such as metals, other polymers and to itself. Finally, the incorporation of fluorine into the polymer increases the solubility of the polymer and therefore decreases the development time.

10 In addition, the use of N-methyldiethanolamine dimethacrylate doubles the number of photoreactive groups for each carboxylate group and improves the photospeed. Since less acrylate monomer is present in the formulation, the properties of the cured polyimide are correspondingly 15 improved.

Typical uses for the composition are as protective coatings for semiconductors, dielectric layers for multilayer integrated circuits, high temperature solder mask, bonding multilayer circuits, a final passivating 20 coating on electrical electronic devices and the like.

#### Photoresist Performance Testing

##### Spray Development Rate

25 A 4-inch silicon wafer with a silicon dioxide coating is coated with the photosensitive solution by spin coating at approximately 2000 rpm for 30 seconds. The wafer is prebaked on a hot plate at 90°C for 3-10 minutes to remove solvent and provide a 20 microns thick film. The coated 30 wafer is patterned on a Oriel contact printer with a 500 watt mercury broad band light source having a 8-15mW/cm<sup>2</sup> intensity, for approximately 25 seconds, using a Optiline 4000-F5 multidensity resolution mask. A 30 second, 60°C post exposure bake follows.

35 Wafer spray development is performed using a Solitec negative developer track with a N-methylpyrrolidone,

methanol, water (62/33/5 weight ratio) solution or 70/30 gamma-butyrolactone/t-butanol solution, followed by an isopropanol rinse and drying. Development time (seconds) was assessed by the time to completely clear the baked film

5 coated on the silicon wafer. The development rate could be determined from the coating thickness and the development time. Minimum feature resolution was determined by optical microscopy. Film retention was obtained by measuring the ratio of post-developed film thickness to post-baked film

10 thickness after a spray development cycle of 1.25 X the development time.

#### Adhesion

Adhesion to copper was measured by spin coating a

15 clean copper substrate with the photosensitive solution, soft-baking at 83°C for 15 minutes on a hot-plate to remove the solvent, blanket exposing at 500mJ/cm<sup>2</sup> and curing at 350°C for one hour. Adhesion results are given as the percent of the photoresist area that remains adhered

20 without delamination. An adhesion of at least 80 % is considered to be acceptable for most applications.

Self-adhesion was assessed by spin coating a layer of liquid film (layer 2) over material partially cured between 150 and 200°C (layer 1). An "OK" result indicates at least

25 a 10°C operating window between the elimination of solvent cracks at low cure temperatures and loss of adhesion at high cure temperatures. At low partial cure temperatures, layer 1 is not sufficiently cured to withstand solvent attack during the application of layer 2. This attack

30 appears as cracking of the surface of layer 1. At high partial cure temperatures, layer 1 is too thoroughly cured to allow interdiffusion and interaction between layers 1 and 2 for adequate adhesion to develop. These two processes determine whether or not there is a window of

35 operability for self adhesion by the method of partial cure. If there is some temperature at which layer 1 can be

cured such that it does not crack when layer 2 is applied and such that it adheres to layer 2, there is some operable point. For many materials, especially non-fluorinated materials, as temperature increases, cracking disappears at a temperature above which adhesion disappears. This results in no operable point. An operable window of at least 10°C between the point at which cracking disappears and adhesion disappears is considered acceptable for most applications.

10

#### Transparency

The molar extinction coefficient of a soft-baked film was measured at 365nm using a UV spectrometer (20 micrometers thickness). In order to successfully resolve

15 features at the bottom of the film, sufficient exposure energy must be transmitted to the bottom of the film. If the extinction coefficient is too large, very little energy reaches the bottom of the film. When this condition exists, sufficient exposure of the bottom region of the  
20 film results in over-exposure of the upper regions of the film. For the final formulation, there are two components of the extinction coefficient of the mixture; first there is the contribution from the polymer backbone. This needs to be kept below  $5 \times 10^4 /m$  at the exposure wavelength for  
25 most applications. After the formulation with the photopackage, the extinction coefficient needs to be kept between  $8 \times 10^4$  and  $1.5 \times 10^5 /m$  for optimum performance.

#### Dielectric Constant

30 The dielectric constant was measured according to ASTM-D150 by parallel plate capacitance .

#### Moisture Absorption

35 Moisture absorption was measured using a quartz microbalance as equilibrium weight gain at 25°C and 85% relative humidity according to D. C. Bonner and Y. Chang

Journal - Polymer Science, Polymer letters, Vol. 13,  
Pg. 259, 1975.

The following examples serve to illustrate certain  
embodiments of the herein disclosed invention. These  
5 examples should not, however, be construed as limiting the  
scope of the invention, as there are many variations which  
may be made thereon without departing from the spirit of  
the disclosed invention, as those of skill in the art will  
recognize.

10

#### GLOSSARY

BPDA	3,3',4,4'-biphenyltetracarboxylic dianhydride
BTDA	3,3',4,4'-benzophenone tetracarboxylic 15 dianhydride
PPD	p-phenylene diamine
6FDA	2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride
MPD	m-phenylene diamine
20 ODA	4,4'-diaminodiphenyl ether
DADS	4,4'-diaminodiphenyl sulfone
ODPA	oxydiphtalic dianhydride
HAB	4,4'-diamino-3,3'-dihydroxybiphenyl
NMP	N-methyl pyrrolidone
25 MADEMA	N-methyldiethanolamine dimethacrylate
6FDAM	2,2-bis(4-aminophenyl)hexafluoropropane
BDAF	2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoro- propane
DABTF	3,5-diaminobenzotrifluoride
30 OBABTF	4,4'-oxy-bis[3-(trifluoromethyl)benzenamine]
PMDA	pyromellitic dianhydride
HEMA	hydroxyethyl methacrylate
APB134	1,3-bis(4-aminophenoxy)benzene

35

#### Examples 1 to 16

(Comparative Examples 1A, 2A, 7A, 7B, 9A to 9D and 11A)

Poly(amic carboxylate salt) Preparation

Commercially available dianhydride and diamine monomers were used without further purification. From 0.1 to 0.4 part by weight of anhydride and diamine monomers (see Table I) were polymerized in 1 part by weight of NMP solvent. The monomers were used in a molar ratio of from 0.8 to 1.0 and 1.0 to 0.8 of dianhydride to diamine, preferably from 0.98 to 1.0 diamine to dianhydride. The reaction mixture was stirred at 25°C to complete the polymerization and form a solution of the poly(amic acid) in NMP.

MADEMA was added to the poly(amic acid) solution in a molar ratio of 0.1 to 1.0, based on the total molar amount of monomers, to form a photosensitive poly(amic carboxylate salt).

Formulation of Photosensitive Composition

The following ingredients were added to the poly(amic carboxylate salt) solution to form a photosensitive composition for coating as a photoresist:

		<u>WT./WT. POLYMER</u>
(a) Sensitizer	Coumarin 314T	0.005
(b) Initiator	1-phenyl-1,2-propane-dione-2-(o-ethoxy-carboxyl)oxime	0.07
(c) Hydrogen Donor	2-benzoxazolethiol	0.06
(d) Stabilizer	1,4,4-trimethyl-2,3-diazabicyclo (3.2.2)-non-2-ene-2,3-dioxide	0.002
(e) IPN former	tetraethylene glycol diacrylate	0.20

(d) Adhesion promoter	triethoxy silyl propyl urea	0.02
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Application and Processing  
of Photosensitive Composition

A 4-inch silicon wafer with a silicon dioxide coating  
5 was coated with the photosensitive solution by spin coating  
at approximately 2000 rpm for 30 seconds. The coated wafer  
was prebaked on a hot plate at 90°C for 3-10 minutes to  
remove solvent and provide a 20 microns thick film. The  
coated wafer was patterned on an Oriel contact printer  
10 Model No. \_\_\_\_\_ with mercury broad band light source at 8-  
15mW/cm<sup>2</sup> intensity for approximately 25 seconds, using an  
Optiline 4000F5 multidensity resolution mask. A 30 second,  
60°C post exposure bake followed.

Wafer spray development was performed on a Solitec  
15 negative developer track using an NMP, methanol, water  
(62/33/5 wt./wt. %) solution or 70/30 gamma-  
butyrolactone/t-butanol solution, followed by an  
isopropanol rinse and drying. Development rate was  
determined by film thickness measurement. Pattern  
20 resolution was determined by optical microscopy.

Film retention was obtained versus exposure dose using  
a profilometer. Results are summarized in Table I.

The photosensitive compositions of the invention,  
which are derived from poly(amic acid)s containing fluorine  
25 and which are at least partially neutralized with methyl  
diethanolamine dimethacrylate (see Examples 1, 2, 7, 9 and  
11), generally have superior metal and self-adhesion,  
faster development rates and superior image resolution of  
the photoresist, when compared to photosensitive  
30 compositions derived from poly(amic acid)s which do not  
contain fluorine (comparative Examples 1A, 2A, 7A, 7B, 9A-D  
and 11A).

Particularly preferred herein, is a photosensitive composition derived from 2,2-bis(3,4'-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 4,4'-diaminodiphenylether (ODA) neutralized with 5 N-methyldiethanolamine dimethacrylate (MADEMA), which also exhibits increased transparency together with low moisture absorption and dielectric constant, as can be seen from the results given in Table II.

TABLE I  
MONOMER EFFECT ON SPRAY DEVELOPMENT  
RATE AND RESOLUTION

EXAMPLE NO.	MONOMERS (MOLE %)	MADEMA % NEUTRAL- IZATION	COPPER	SELF- ADHESION
			(%)	
1	6FDA(100)/ODA(100)	100	100	OK
1A	BPDA(100)/PPD(100)	25	0	NG
2	BPDA(70)/6FDA(30)/PPD(70)/ODA(30)	25	98	
2A	BPDA(70)/BTDA(30)/PPD(70)/ODA(30)	25	50	
3	BPDA(100)/HAB(75)/6FDAM(25)	25	86	NG
4	BPDA(100)/HAB(65)/6FDAM(35)	25	98	NG
5	BPDA(85)/6FDA(15)/PPD(100)	25	0	NG
6	BPDA(60)/6FDA(40)/PPD(100)	25	100	NG
7	BPDA(70)/6FDA(30)/PPD(100)	25	96	NG
7A	BPDA(70)/ODPA(30)/PPD(100)	25	10	
7B	BPDA(70)/BTDA(30)/PPD(100)	25	0	NG
8	BPDA(85)/6FDA(15)/PPD(70)/HAB(30)	25	84	OK
9	BPDA(100)/PPD(70)/6FDAM(30)	25	100	OK
9A	BPDA(100)/PPD(70)/DADS(30)	25	10	
9B	BPDA(100)/PPD(70)/MPD(30)	25	5	
9C	BPDA(100)/PPD(30)/MPD(70)	25	0	
9D	BPDA(100)/PPD(70)/ODA(30)	25	10	
10	BPDA(100)/HAB(55)/6FDAM(45)	25	100	OK
11	BPDA(100)/PPD(70)/BDAF(30)	25	100	NG
11A	BPDA(100)/PPD(70)/APB134(30)	25	0	NG
12	BPDA(100)/PPD(70)/DABTF(30)	25	0	OK
13	BPDA(100)/PPD(70)/OBABTF(30)	25	90	OK
14	BPDA(100)/PPD(90)/6FDAM(10)	25	0	NG
15	BPDA(75)/6FDA(25)/PPD(100)	25	0	OK
16	BPDA(80)/6FDA(20)/PPD(100)	25	0	OK

TABLE I (Continued)

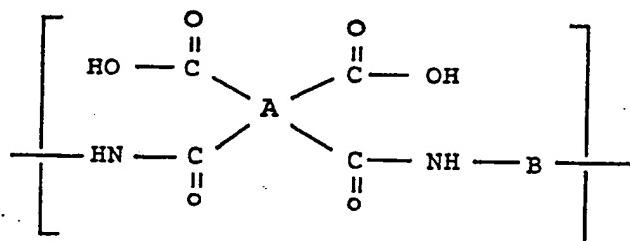
EXAMPLE NO.	MONOMERS (MOLE %)	DEVELOP.			
		DEVELOP. TIME [SECOND]	RATE (μm/ [SECOND])	FILM RETENTION (%)	RESOLUTION (μm)
1	6FDA(100)/ODA(100)	15	1.33	98	10
1A	BPDA(100)/PPD(100)	440	0.05	92	10
2	BPDA(70)/6FDA(30)/PPD(70)/ODA(30)				
2A	BPDA(70)/BTDA(30)/PPD(70)/ODA(30)				
3	BPDA(100)/HAB(75)/6FDAM(25)				
4	BPDA(100)/HAB(65)/6FDAM(35)				
5	BPDA(85)/6FDA(15)/PPD(100)				
6	BPDA(60)/6FDA(40)/PPD(100)	163	0.12	94	
7	BPDA(70)/6FDA(30)/PPD(100)	133	0.15	94	
7A	BPDA(70)/ODPA(30)/PPD(100)				
7B	BPDA(70)/BTDA(30)/PPD(100)				
8	BPDA(85)/6FDA(15)/PPD(70)/HAB(30)				
9	BPDA(100)/PPD(70)/6FDAM(30)				
9A	BPDA(100)/PPD(70)/DADS(30)				
9B	BPDA(100)/PPD(70)/MPD(30)				
9C	BPDA(100)/PPD(30)/MPD(70)				
9D	BPDA(100)/PPD(70)/ODA(30)				
10	BPDA(100)/HAB(55)/6FDAM(45)	276	0.07	66	
11	BPDA(100)/PPD(70)/BDAF(30)				
11A	BPDA(100)/PPD(70)/APB134(30)				
12	BPDA(100)/PPD(70)/DABTF(30)				
13	BPDA(100)/PPD(70)/OBABTF(30)	421	0.05	90	
14	BPDA(100)/PPD(90)/6FDAM(10)				
15	BPDA(75)/6FDA(25)/PPD(100)				
16	BPDA(80)/6FDA(20)/PPD(100)				

TABLE II

<u>COMPOSITION</u>	<u>EXTINCTION COEFFICIENT <math>m^{-1} @ 365nm</math></u>	<u>DIELECTRIC CONSTANT @ 1MHz, 50% RH</u>	<u>MOISTURE ABSORPTION WT/WT % @ 85% RH</u>
6FDA/ODA/MADEMA (EXAMPLE 1)	1.1 X 10 <sup>5</sup>	3.0	2.7
BPDA/PPD (EXAMPLE 1A)	1.0 X 10 <sup>6</sup>	2.9	1.5
PMDA/ODA	2.5 X 10 <sup>5</sup>	3.5	3.6
6FDA/ODA	2.8 X 10 <sup>4</sup>	2.7	2.0
BTDA/ODA/MPD/HEMA	3.9 X 10 <sup>5</sup>	3.3	3.7

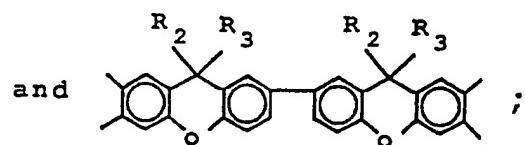
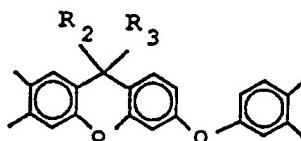
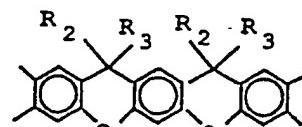
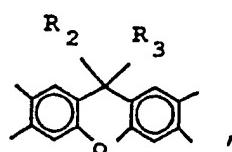
What is claimed is:

1. A photosensitive composition comprising:
  - (a) an aprotic solvent;
  - (b) a photosensitizing component;
  - (c) a fluorinated poly(amic acid) polymer containing a repeating unit of the formula



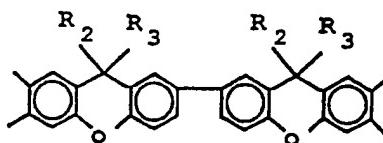
10

wherein A is a tetravalent organic radical selected from the group consisting of

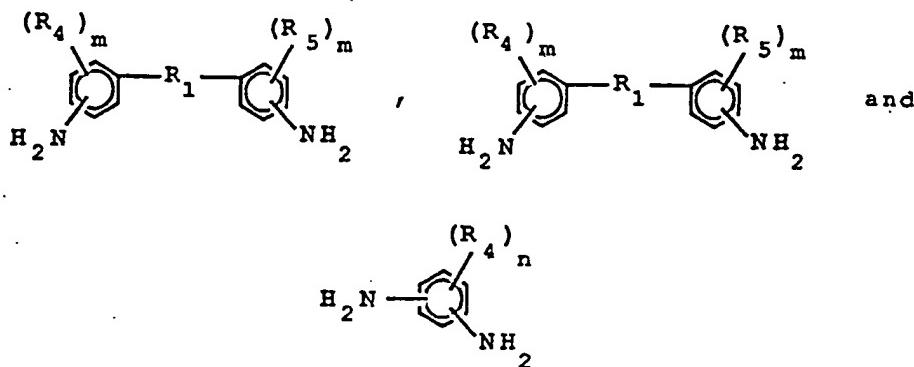


15

and



and B is a divalent radical of an aromatic diamine selected from the group consisting of



wherein R<sub>1</sub> is -CH<sub>2</sub>-, -C<sub>2</sub>H<sub>4</sub>, -C(CF<sub>3</sub>)<sub>2</sub>-,  
-<sub>C4-7</sub>F<sub>8-14</sub>-, -S-, -SO<sub>2</sub>-, -O-, -CO-,  
5 R<sub>6</sub>, -O-R<sub>6</sub>-O-, -O-R<sub>6</sub>-C(CF<sub>3</sub>)<sub>2</sub>-R<sub>6</sub>-O-,  
-O-R<sub>6</sub>-C(CH<sub>3</sub>)<sub>2</sub>-R<sub>6</sub>-O-, -O-R<sub>6</sub>-SO<sub>2</sub>-R<sub>6</sub>-O-,  
-O-R<sub>6</sub>-O-R<sub>6</sub>-O-, -O-R<sub>6</sub>-CO-R<sub>6</sub>-O-,  
-O-R<sub>6</sub>-CO-R<sub>6</sub>-CO-R<sub>6</sub>-O-, -O-R<sub>6</sub>-R<sub>6</sub>-O-, -CO-R<sub>6</sub>-CO-,  
-CO-R<sub>6</sub>-O-R<sub>6</sub>-CO- or -O-R<sub>6</sub>-SO<sub>2</sub>-R<sub>6</sub>-O-;

10

R<sub>2</sub> and R<sub>3</sub> are phenyl, C<sub>1-4</sub> alkyl,  
C<sub>1-4</sub> perfluoralkyl, C<sub>1-4</sub> perfluoroalkoxy,  
C<sub>1-4</sub> perfluoroalkylphenyl or -OC<sub>1-6</sub> alkylene-  
OC<sub>1-6</sub> perfluoroalkyl;

15

R<sub>4</sub> and R<sub>5</sub> are H, Cl, F, C<sub>1-4</sub> alkyl, OH;  
C<sub>1-8</sub> perfluoroalkyl or C<sub>1-8</sub> perfluoroalkoxy;

R<sub>6</sub> is



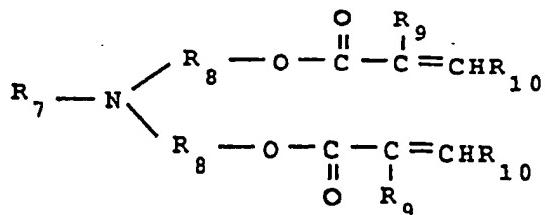
20

m is 0 to 4; and

n is 0 to 3; and

25

- (d) a tertiary amine di(meth)acrylate having the formula



wherein R<sub>7</sub> is C<sub>1</sub>-6 alkyl or C<sub>1</sub>-3 cycloalkyl;  
 5 R<sub>8</sub> is C<sub>2</sub>-12 alkylene or C<sub>3</sub>-6 cycloalkylene;  
 R<sub>9</sub> is H or C<sub>1</sub>-2 alkyl; and R<sub>10</sub> is H or aryl,

wherein said tertiary amine di(meth)acrylate is present in an amount sufficient to neutralize from 10 to 100 mole % of said poly(amic acid) polymer.

10

2. The photosensitive composition of Claim 1 wherein the tertiary amine di(meth)acrylate is N-methyldiethanolamine dimethacrylate.

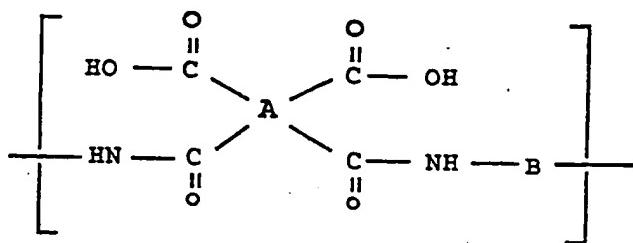
15 3. The photosensitive composition of Claim 2 wherein the fluorinated poly(amic acid) polymer comprises 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane and 4,4'-diaminodiphenyl ether.

20 4. The photosensitive composition of Claim 2 wherein the fluorinated poly(amic acid) polymer comprises 3,3',4,4'-biphenyltetracarboxylic dianhydride, p-phenylene diamine and 4,4'-oxy-bis[3-(trifluoromethyl)-benzenamine].

25 5. An electronic device comprising an electronic component selected from the group consisting of a conductor, a semiconductor and an insulator; and a polyimide film deposited thereon, said polyimide having been formed from a poly(amic acid) precursor comprising:

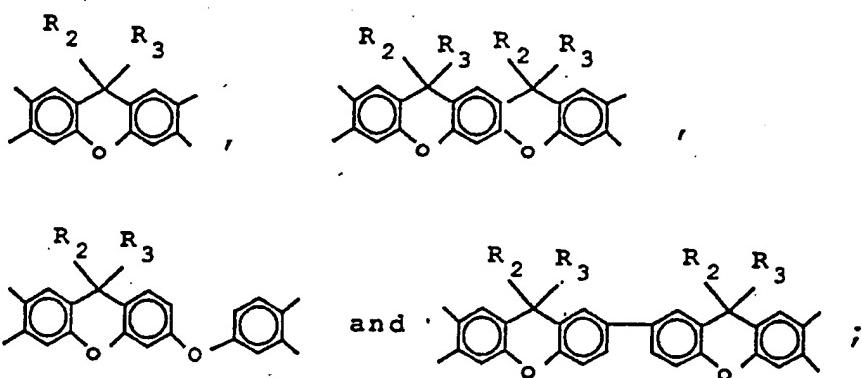
- (a) an aprotic solvent;
- (b) a photosensitizing component;
- (c) a fluorinated poly(amic acid) polymer containing a repeating unit of the formula

30

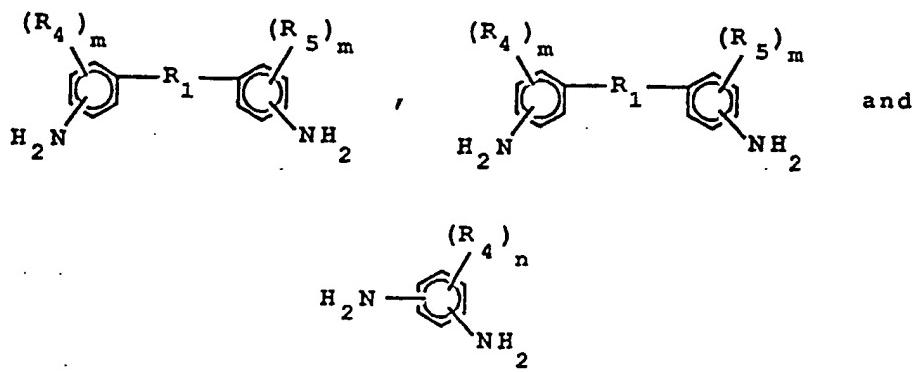


wherein A is a tetravalent organic radical selected from the group consisting of

5



and B is a divalent radical of an aromatic diamine selected from the group consisting of



10

wherein R1 is  $-\text{CH}_2-$ ,  $-\text{C}_2\text{H}_4-$ ,  $-\text{C}(\text{CF}_3)_2-$ ,

$-C_4-7F_8-14-$ , -S-, -SO<sub>2</sub>-, -O-, -CO-,  
 R<sub>6</sub>, -O-R<sub>6</sub>-O-, -O-R<sub>6</sub>-C(CF<sub>3</sub>)<sub>2</sub>-R<sub>6</sub>-O-,  
 -O-R<sub>6</sub>-C(CH<sub>3</sub>)<sub>2</sub>-R<sub>6</sub>-O-, -O-R<sub>6</sub>-SO<sub>2</sub>-R<sub>6</sub>-O-,  
 -O-R<sub>6</sub>-O-R<sub>6</sub>-O-, -O-R<sub>6</sub>-CO-R<sub>6</sub>-O-,  
 -O-R<sub>6</sub>-CO-R<sub>6</sub>-CO-R<sub>6</sub>-O-, -O-R<sub>6</sub>-R<sub>6</sub>-O-, -CO-R<sub>6</sub>-CO-,  
 -CO-R<sub>6</sub>-O-R<sub>6</sub>-CO- or -O-R<sub>6</sub>-SO<sub>2</sub>-R<sub>6</sub>-O-;

R<sub>2</sub> and R<sub>3</sub> are phenyl, C<sub>1-4</sub> alkyl,  
C<sub>1-4</sub> perfluoralkyl, C<sub>1-4</sub> perfluoroalkoxy,  
C<sub>1-4</sub> perfluoroalkylphenyl or -OC<sub>1-6</sub> alkylene-  
OC<sub>1-6</sub> perfluoroalkyl;

R4 and R5 are H, Cl, F, C<sub>1-4</sub> alkyl, OH; C<sub>1-8</sub> perfluoroalkyl or C<sub>1-8</sub> perfluoroalkoxy;

15

R<sub>6</sub> is

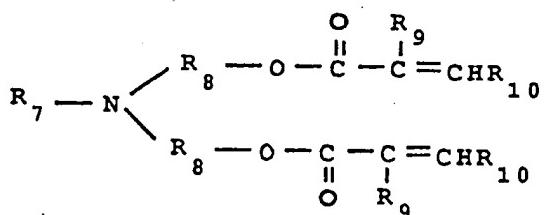


m is 0 to 4; and

20                   n is 0 to 3; and

(d) a tertiary amine di(meth)acrylate having the formula

25



wherein R<sub>7</sub> is C<sub>1-6</sub> alkyl or C<sub>1-3</sub> cycloalkyl;  
R<sub>8</sub> is C<sub>2-12</sub> alkylene or C<sub>3-6</sub> cycloalkylene;  
R<sub>9</sub> is H or C<sub>1-2</sub> alkyl; and R<sub>10</sub> is H or aryl.

wherein said tertiary amine di(meth)acrylate is present in an amount sufficient to neutralize from 10 to 100 mole % of said poly(amic acid) polymer.

5       6. The electronic device of Claim 5 wherein the tertiary amine di(meth)acrylate is N-methyldiethanolamine dimethacrylate.

10      7. The electronic device of Claim 6 wherein the fluorinated poly(amic acid) polymer comprises 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane and 4,4'-diaminodiphenyl ether.

15      8. The electronic device of Claim 6 wherein the fluorinated poly(amic acid) polymer comprises 3,3',4,4'-biphenyltetracarboxylic dianhydride, p-phenylene diamine and 4,4'-oxy-bis[3-(trifluoromethyl)-benzenamine].

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 94/08519

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 G03F7/038 G03F7/004

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>DATABASE WPI Section Ch, Week 9122, Derwent Publications Ltd., London, GB; Class A89, AN 91-158479 &amp; JP,A,3 091 752 (SUMITOMO BAKELITE KK) 17 April 1991 cited in the application see abstract</p> <p>---</p> <p>EP,A,0 475 086 (HITACHI, LTD.) 18 March 1992 see page 2, line 3 - line 5 see page 31, line 9 - line 13 see page 16, line 16 - line 17 see page 21 - page 22; example 20</p> <p>---</p> <p>-/-</p>	1-8
Y		1-8

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
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- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- \*&\* document member of the same patent family

Date of the actual completion of the international search

16 November 1994

Date of mailing of the international search report

01.12.94

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## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 94/08519

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JOURNAL OF APPLIED POLYMER SCIENCE, vol.38, no.3, 5 August 1989, NEW YORK pages 389 - 402, XP372018 T. OMOTE, T. YAMAOKA, K. KOSEKI 'Preparation and Properties of Soluble and Colorless Fluorine-Containing Photoreactive Polyimide Precursors' see page 401 -----	1-8

1

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

**PCT/US 94/08519**

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0475086	18-03-92	JP-A-	4120542	21-04-92